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#### PHYSICOCHEMICAL PROPERTIES OF BORON-CARBON ALLOYS

The molten system of boron and carbon has been studied several times previously in particular in relation to its extreme hardness and corrosion resistance. In 1954, Ridgway<sup>1</sup> has carried out the x-ray analysis of boron carbide powders ( $B_4C$ ). He also determined melting points, specific resistances, coefficient of linear expansion as well as a series of hardness tests characteristic to this compound.

Systematic analysis of the phase diagram for the boron carbide system was started by Ormont<sup>2</sup> in 1939 and was further reported in a later work<sup>3</sup>. In this latter analysis the region in a phase diagram in the limits of carbon content from 10-50% by weight was determined. It was also found (established) that the boron carbide is formed by the reversible reaction:  $(B + [liquid\ phase,\ rich\ in\ carbon] = B_4C)$  and the presence of eutectic composition at (30.8% C) was shown. It was supposed that the above eutectic was between boron carbide and carbon phases. G. C. Zhdanov<sup>4</sup>, et al have studied the structure of boron carbide and have established that it consists of a rhombohedral crystalline cell with  $a = 5.60$  and  $c = 12.1\text{ \AA}$ .

In 1953, Zhdanov, et al<sup>5</sup> have proposed a hypothesis in which they postulated that substances with covalent bonds may form solid solutions under conditions of preserving the directional character of the covalent bonds. In particular, in case of boron carbide, some replacement of the portion of carbon atoms in the (1 b) position of boron atoms which, possessing  $sp$ -electrons, may form a linear valence configuration similar to carbon atoms.

Detailed analysis of this question<sup>6</sup> has shown that such displacement of carbon atoms in  $B_{12}C_8$  ( $=B_4C$ ) with the formation of  $B_{12}C_9$  actually takes place; it was also possible to determine the crystal cell distances in the  $B_4C$  crystal with greater precision. The following values were obtained:  $a = 4.496 \pm 0.002\text{ \AA}$ ,  $c = 12.12 \pm 0.002\text{ \AA}$ . Certain physical and chemical characteristics of the  $B_{12}C_9$  carbide were obtained.

Glaser, et al<sup>7</sup> have carried out an x-ray analysis as well as determination of specific gravity and resistance of the boron-carbon melts in the region from 4-60 mole % carbon. These authors show that the interatomic distances in the crystalline phases as well as the specific gravities of these solid solutions continuously increases while the electrical resistance in these solid solutions decreases in the region of 4-38 mole % carbon. This observation allowed the authors to postulate a continuous series of solid solutions of carbon in boron in the region of concentration that were studied.

-2-

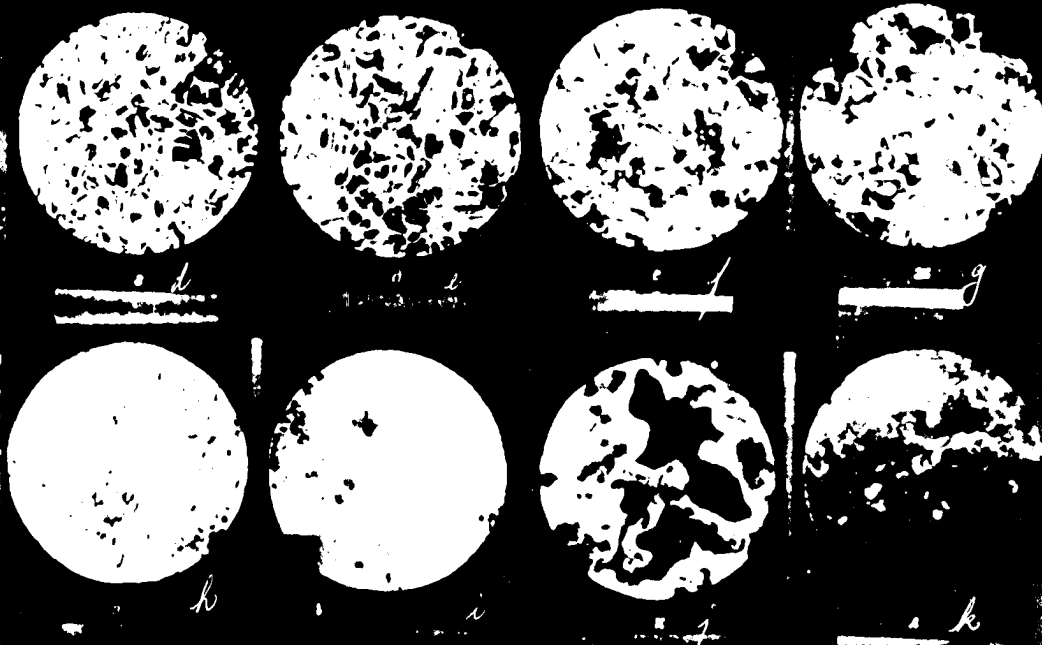
Finally, Allen<sup>6</sup> has studied the interatomic distances and specific gravities of melts that may be described by empirical formulas  $B_2C$ ,  $B_3-ccC$ ,  $B_7C$  and has shown the possibility of displacement of carbon atoms by boron atoms in the solid solution as well as formation of excess boron and carbon molten solutions by the process of infiltration into the existing boron-carbon crystalline shell. The divergence of the available data on the properties of solid solutions of boron in carbon have shown the necessity for further study of such solutions.

During the preparation of boron-carbon solid solutions, the authors used highly refined amorphous boron of 99.7% purity and highly refined lampblack containing 99.8% carbon. These pure boron and carbon samples were mixed in desired ratios so that the following compositions were obtained as expressed in terms of carbon 5, 8, 10, 13, 15, 18, 20, 30, 40, 50, 60, 70 mole % (5.6, 8.6, 10.95, 14.14, 16.36, 19.59, 21.75, 32, 42.4, 52.8, 62.2, 72.8 weight %). These mixtures were then sintered and hot-pressed, using the method analogous to the one described by Glaser<sup>7</sup>. It was found that the melt consisting of 5 mole % carbon in boron had a lower melting point than that of pure boron (2075°C). The chemical analysis of resulting molten compositions have shown the change in their carbon content so that the actual determined composition of the resulting melts were: 5.11, 9.95, 12.71, 15.89, 17.47, 22.85, 24.67, 33.97, 42.20, 52.60, 62.20, 72.20 weight % carbon. The obtained sintered samples of the above boron-carbon compositions were further treated in a vacuum furnace in order to eliminate internal strains and to insure homogeneity of each sample. This treatment was followed by slow cooling of each sample to room temperature. Samples for metallographic analysis were prepared from the surfaces by a diagonal cut of each vacuum heat treated sample by the method described by Sumenov<sup>8</sup>.



Figure 1. Microstructure of the boron-carbon alloy samples (magnification (X600)) Alloy compositions in % C. a - 5.11% before heat treatment, b - 5.11% after heat treatment, c - 9.95%.

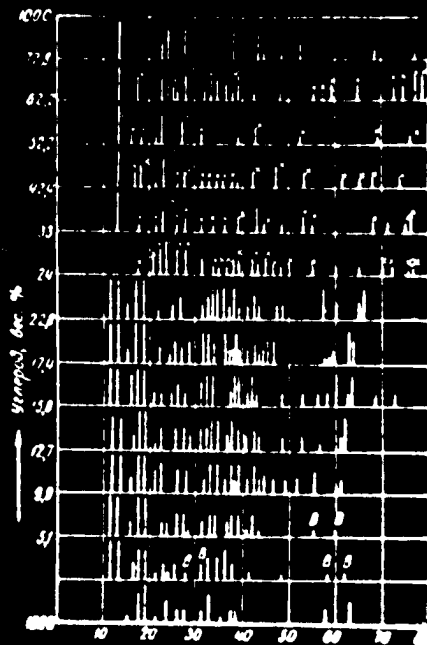
- 3 -



d - 15.89%, e - 17.47%, f - 22.38%, g - 24.07%, h - 33.97%, i - 42.50%  
j - 52.60%, k - 62.50%.

In figure 1 we show the structure of certain samples of boron-carbon alloys. The sample containing 5.11% C before heat treatment exhibits a polyhedral structure while after heat treatment one notices the appearance of needle like crystals presumably denoting a eutectic alloy. With the rise in the carbon content of the boron carbon samples 9.93% C the crystalline character, comprising up to 70% of the sample area, tends to lose the needle like crystalline appearance and becomes polyhedral in its character. It is necessary to note that the structure of the alloys containing from 9.93-24.07 weight % carbon is similar before and after the vacuum heat treatment. Starting with 12.71 weight % carbon one notices a certain amount of duplication somewhat diminishing only in a sample containing 24.07% C. However a portion of the above mentioned crystalline sample does not exhibit duplication and has a bright surface which presumably testifies to the presence of two types of crystalline species. In the micrograph of the sample containing 33.97% C a crystalline eutectic is noted. (see figure 1 h) Upon further increase of the carbon content of boron-carbon alloy samples a new phase appears on the eutectic background. The maximum amount of this phase was noted in a sample containing 62.50% C. All the samples, after photomicrographic analysis, were crushed to a fine powder and then subjected to the x-ray analysis which were carried out with copper source and nickel filter. The results of the x-ray analysis are shown graphically in figure 2.

Figure 2. X-ray diagrams of B-C systems; C is carbon lines; \* Boron lines;  $\Delta$  of new phase  $B_nC_m$ ; other lines belong to  $B_2C$  structure.



The study of the x-ray diagram shows that even a B-carbon melt containing as little as 5.11% C exhibits a different pattern indicating a crystalline structure different from pure boron. The structure of the main phase of this melt may be described as a structure of a new boron-carbide ( $B_{12}C_6$  or  $B_{12}C_7$ ).

In the sample containing 5.11% C along with the lines pertaining to boron carbide ( $B_2C$ ) one also notes lines of pure boron which in conjunction with the data obtained from microphotographic analysis allows to postulate the presence of solid solution of carbon in boron along with the conventional boron carbide ( $B_2C$ ). Up until the 22.85 weight % carbon the samples of melts contain only the  $B_2C$  lines. With the sample containing 24.07 weight % carbon the x-ray diagram character is changed. However the characteristic doublet of boron carbide does not disappear. Further increase in the boron content leads to a sharp change in the structure of the alloys. Along with the lines of free boron one notes the appearance of a number of new lines which are most noticeable in the x-ray diagram of the melt containing 72.5% C.

For determination of specific gravities of powdered samples of the boron-carbon melts pycnometric method of analysis was used with xylene. The resulting data listed in Table 2 and are plotted in Figure 3. It can be seen from these data that the specific gravity of the boron-carbon melts increased to the maximum 20% carbon after which it begins to decline. These data therefore confirm the

- 5 -

date of Glaser<sup>7</sup>. The microhardness of melts, measured with the aid of the PMT-3 apparatus using a 40 gram load (see table 3 and figure 3) also increases as a function of carbon contents (from 5.11-17.47% C) after which it drops rapidly. The microhardness of the main phase in a system containing 42.5% C is of the same order of magnitude as that of the boron-carbide containing 17.47% C.

PHYSICAL PROPERTIES OF BORON-CARBON SYSTEM

Carbon Content Weight%	Density gm/cm <sup>3</sup>	Microhardness Kg/mm <sup>2</sup>	Electric Resistance ohm/cm
5.11	2.310	2995 ± 443	1.64 · 10 <sup>-1</sup>
9.93	2.400	3042 ± 497	
12.71	2.458	3580 ± 501	4.95 · 10 <sup>-1</sup>
15.89	2.531	4460 ± 843	3.14
17.47	2.548	3108 ± 463	
22.83	2.456	4252 ± 427	4.36
24.07	2.503	2790 ± 117	7.13
33.97	2.37	-	
42.5	2.31	-	1.2
52.6	2.47	4430 ± 435	0.8
62.5	2.10	-	
72.5	2.08	-	

Electrical resistance of the boron carbide samples containing 5.11% carbon falls rapidly in comparison with the electrical resistance of pure boron after which it increases reaching a maximum in the melt containing 24.07% carbon.

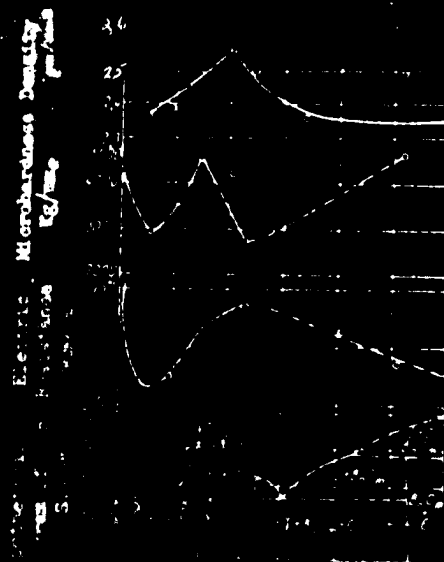


Fig. 3. Electrical resistance, density and microhardness of boron carbon alloy samples as a function of carbon content.

- 6 -

The character of the change in the electrical resistance of the boron carbon alloy samples with the increase in their carbon content allows to postulate following hypothesis. The electrical resistance of boron is in the order of  $7.7 \times 10^5$  ohm/cm, which may be accounted for, supposedly, by the complete compensation of all the valence bonds of boron atoms in the boron crystal. Upon addition of certain amounts of carbon to boron there occurs a change in the structure of the crystalline unit cell which, however, leaves some unsatisfied -C-C- bonds which would account for appearance of a certain amount of electrical conductivity. With further addition in the carbon content of some of the boron carbon alloys these unsatisfied -C-C- bonds are compensated and form conventional covalent bonds, common to the conventional boron carbide crystal, this in turn of course leads to the increase in the electrical resistance. The maximum resistance corresponds to the completely satisfied boron carbon matrix with the conventional, directional, covalent bonds of the boron carbide crystal ( $B_4C$ ). The electrical resistance determined on the 24.07% C sample of boron carbide is of the same order of magnitude with the value that Ridgway lists for the samples of boron carbide that he studied. (4.15 and 4.45 ohm/cm). Summarizing the data obtained in this work, it is possible to draw the following conclusions.

Upon addition of carbon to boron in the amount of 2-3% a eutectic is formed containing boron or a solid solution of carbon in boron with boron carbide  $B_{13}C_2$ , which contains as the results obtained from determination of microhardness, density and electrical resistance, an imperfect crystalline structure, that is, vacant spaces in the -C-B-C- of the boron carbide  $B_{13}C_2$ .

Upon further increase in the carbon content of the boron-carbon alloys there occurs a gradual "filling-in" of the vacancies in the crystal shell until the carbon content reaches the level equivalent of the carbon content in  $B_{13}C_2$ . Boron carbide  $B_{13}C_2$  is in turn capable of forming solid solutions with carbon eventually forming the  $B_{12}C_3$  carbide (that is, forming -C-C-C- in addition to -C-B-C- bonds). This latter carbide forms eutectic compositions with the carbide  $B_4C$ , which is richer in carbon than  $B_4C$  and which has a tentative formula  $BC_3$ . This carbon rich boron carbide material (eutectic) is the product of the following reaction,  $B_{12}C_3 \rightleftharpoons B_4C + C$ , which is reversible and is usually accompanied by formation of free carbon. On the basis of the above hypothesis we have constructed a phase diagram describing the boron carbon system containing up to 60-70% carbon shown in Figure 3. It has to be noted that this system satisfactorily agrees with the data described in earlier works pertaining to the study of boron carbides.

#### CONCLUSIONS

1. An x-ray and a photomicrographic study of the boron carbon system has been made which includes determinations of electrical resistance and densities of the boron-carbon melts in the region of carbon content from 5 to 72.5 weight percent carbon. In this study we show that with the 5% carbon and higher content in the boron-carbon melts there is produced a defective crystalline structure of boron carbide  $B_{13}C_2$  which is characterized by the presence of vacancies in the -C-C-C- along the crystal axis of  $B_{13}C_2$ . In the 14-16% carbon containing melts these vacancies are filled with the additional carbon atoms forming the -C-B-C- structure, which is then further changed to the -C-C-C- structure in the  $B_{12}C_3$  ( $B_4C$ ) boron carbide. The melts containing the defective crystalline structure of  $B_{13}C_2$  possess a considerable amount of electric conductivity which is dependent on the amount of vacancies occurring along the C axis.

- 7 -

2. On the basis of previously obtained data and also results obtained in this present work an attempt was made to depict a hypothetical phase diagram for the boron-carbon system.

#### LITERATURE

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